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EFFECTS OF SULPHIDE OXIDATION ON SELECTED SOIL PROPERTIES*

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Abstract

This study covered soils containing sulphides (*Potential Acid Sulphate Soils - PASS*), located on Karsiborska Kępa Island (NW Poland). The aim was to analyse changes in some soil properties caused by the oxidation of sulphides to sulphates for developing a new methodology. Soil samples taken from one representative pedon were oxidized under laboratory conditions for 8 weeks (incubation method). During this period the concentration of sulphates and pH in the soil extract was measured at multi-day intervals. Soil organic horizons characterized by a relatively high content of total sulphur (> 0.75%) showed no decrease in pH below 4 due to the oxidation. The opposite was observed in the case of sandy horizons, poor in sulphur. The rate of pH decline during incubation was the highest in the initial period of oxidation, which justifies the need to perform some soil analyses in samples of fresh /wet soil within 48 hours of sampling. The results enabled us to propose a procedure for soils containing sulphides, which included both field and laboratory tests, with special care taken to preserve as much as possible the natural reducing environment.

Key words: potential acid sulphate soils, iron sulphides, oxidation, soil acidification.

WPŁYW UTLENIANIA SIARCZKÓW NA WYBRANE WŁAŚCIWOŚCI GLEB

Abstrakt

Badania dotyczyły gleb zawierających siarczki (*ang. Potential Acid Sulphate Soils - PASS*), zlokalizowanych na wyspie Karsiborska Kępa (wsteczna delta Świny). Celem badań było określenie zmian, jakie zachodzą w glebach przy przejściu od środowiska redukcyjnego do utleniającego, pod kątem opracowania propozycji nowej procedury badawczej. Prace takie w odniesieniu do PASS występujących w Polsce nie były dotychczas prowadzone.

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Zgodnie ze standardami międzynarodowymi pobrane próbki glebowe poddano 8-tygodniowej inkubacji (utlenianiu) w warunkach laboratoryjnych. W trakcie tego okresu wykonywano w kilkudniowych odstępach oznaczenia stężenia siarczanów, a także pomiar pH gleby.

Poziomy organiczne charakteryzujące się relatywnie wysoką zawartością siarki całkowitej (> 0,75) po utlenieniu nie wykazywały spadku pH poniżej 4. Odwrotny efekt obserwowano natomiast w przypadku poziomów piaszczystych ubogich w siarkę. Dynamika spadków wartości pH była największa w początkowym okresie inkubacji, co uzasadnia konieczność wykonania pewnych analiz glebowych w próbkach świeżych/wilgotnych maksymalnie w ciągu 48 h od momentu ich pobrania.

W przedstawionej propozycji metodyki badań PASS, obejmującej zarówno prace terenowe, jak i laboratoryjne, zwrócono szczególną uwagę na możliwie maksymalny stopień zachowywania naturalnie występującego środowisko redukcyjnego.

Słowa kluczowe: gleby zawierające siarczki, siarczki żelaza, utlenianie, kwasowość gleby.

INTRODUCTION

Sulphur is a very important element in soil, because its presence is required for proper physiological functioning of plants (Klikocka 2005). An excess of certain sulphur forms (sulphides, sulphates) in soils alongside some other unfavorable environmental conditions may cause significant losses of agricultural areas. Therefore, sulphurization is a major global problem, which concerns mainly alluvial soils covering a total area of about 17.1 million hectares in the world (Andriesse, Mensvoort 2006). There are two types of acid sulphate soils. In anaerobic conditions, formation of reduced forms of sulphur (sulphides, mainly pyrite) occurs. Soils which will be potentially oxidized if drained are called potential acid sulphate soils (PASS). When these soils are exposed to air due to drainage or some disturbance, sulphuric acid is produced, often releasing toxic quantities of iron, aluminium and heavy metals. Such soils is defined as AASS – Actual Acid Sulphate Soils (Dent, Pons 1995).

In Poland, there are more than 20 sites with PASS and AASS. Most lie in the Polish Baltic coastal zone (Pracz 1989, Pracz, Kwasowski 2001, Nied•wiecki et al. 2002). Several stands have also been found in central and southern Poland (Czerwinski 1996, Hulisz 2007). However, all previous studies mostly focused on the basic recognition of Polish PASS and AASS. A proposal for the classification of these soils was given by Pracz (1989), but unfortunately it has not been included either in the old or the new version of the *Taxonomy of Polish Soils* (1989, 2011). Therefore, further studies aiming at more detailed knowledge of PASS and AASS properties are needed. In the future, it will also be necessary to add a description of these soils to the next version of the Taxonomy of Polish soils.

The aim of this study was to determine changes that occur in different soil samples during the transition from a reducing to an oxidizing environment, and to propose a procedure including both field and laboratory work.

MATERIAL AND METHODS

The field work was carried out in September 2010 in the western part of Karsiborska Kępa Island (NW Poland; 53°51'41″N, 14°19'8″E). The study area is subject to salinization due to backwater effects and seasonal flooding from the Baltic Sea. There are soils formed both under the influence of the Stara Świna river water and seawater (thin peat or muck layers on alluvial subsoils). According to the WRB classification (IUSS Working Group WRB 2007), they can be classified as Histic Fluvisols. It was previously stated that the sulphide oxidation which occurred in these soils could lead to strong acidification. The pH (in H_2O) values determined in oxidized soil samples can be lower than 3.5 (Niedźwiecki et al. 2000, 2002).

In this study, the standard methods for indirect determination of sulphides in soils were used. Thus, it was possible to identify the features typical for PASS (Dent 1980). As the first criterion, which indicated the presence of strongly reducing conditions, voltage (Eh) below 30 mV was adopted (*Guidelines for Soil Description* 2006). In a field study, potential redox (Eh) was measured (potentiometric method) to obtain representative soil samples. The electrical conductivity of bulk soil (EC_a) was also determined by Time Domain Reflectrometry (TDR). The measurements were made at several points (in shallow soil pits). Afterwards, one representative pedon was selected and sampled for further analysis. The soil material (each sample about 500 g), taken from five different horizons, was put in plastic bags to avoid changes in the oxidation-reduction conditions. After the removal of air, the plastic bags are tightly closed. The samples were immediately refrigerated. The first measurements in fresh/wet samples referred to the actual field conditions. Soil extracts were prepared by using ultrapure water saturated with N_2. The following properties were determined: reaction (pH_a in H_2O) by the potentiometric method, SO_4^{2-} ion concentration by the turbidimetric method (the precipitation of sulphates from acidified solution with $BaCl_2$ and photometric measurement of the turbidity of the samples). Moreover, the actual soil moisture was determined by oven drying method. It was necessary to express ion concentrations in relation to absolutely dry soil.

According to the commonly used procedure (Dent 1980, IUSS Working Group WRB 2007, Sullivan et al. 2009), soil samples were placed on plastic trays, creating a layer of about 1 cm thickness, and then incubated at room temperature for a period of 8 weeks (56 days). During this period, the material was sampled in triplicate from each of the horizons for the laboratory analysis (pH in H_2O, SO_4^{2-} concentration and actual moisture). All these analyses were performed on 3, 6, 10, 14, 21, 28 and 56 day of the incubation.

Next, the following properties were determined in air-dry samples (after incubation):

- soil reaction (pH_{pox}) after oxidation with 30% H_2O_2 by the potentiometric method,
- organic carbon (C_{org}), total nitrogen (N_{tot}) and total sulphur (S_{tot}) content using a CNS Variomax analyser.

Based on the results obtained during incubation, the ratio of the concentration of sulphate ions on the different days of analysis ($SO_{4x}{}^{2-}$) to their concentration in the soil sample before incubation ($SO_{4a}{}^{2-}$) was calculated according to the formula:

$$\frac{SO_{4x}{}^{2-}}{SO_{4a}{}^{2-}}$$, where x – the day of analysis.

For interpretation of oxidation-reduction conditions in the soil, the results were transformed to rH values using the formula (IUSS Working Group WRB 2007):

$$rH = 2pH + 2Eh/59$$

The rH values over 35 indicate strongly aerated environment, between 13 and 19 – formation of Fe^{2+}/Fe^{3+} oxides and below 13 – sulphide formation.

The description of the soil horizons was made according to the WRB (*Guidelines for Soil Description* 2006).

RESULTS AND DISCUSSION

Basic soil properties

Potential acid sulphate soils are formed when seawater or sulphate-rich water mixes with waterlogged land sediments containing iron oxides and organic matter in the absence of oxygen (PRACZ 1989, FITZPATRICK et al. 1998). In freshwater environments, soil material oxidation does not usually result in soil acidification because the content of sulphates is too low (LEONARD et al. 1993).

The results of the basic soil analysis are presented in Table 1. The soil was characterized by distinct stratification. Its morphology and properties were formed by both the peat-forming and alluvial processes. The impact of the seawater intrusion was evident. The salinity of the bulk soil (EC_a) ranged from 1.43 to 2.08 dS m^{-1}.

The organic carbon content in the profile (Corg 0.33-34.5%) was related to the presence of mineral (sandy) and organic (mucky, peaty and muddy) horizons. The C:N ratio from 14 to 16 indicated progressive mineralization of organic matter and silting.

The total sulphur content in organic horizons (Ha, Her and Har) varied between 0.78% and 1.93%. It was significantly higher comparing to the average values (0.05-0.67%) found in Polish mineral-organic and organic soils (MOTOWICKA-TERELAK, TERELAK 1998). However, the mineral horizons were characterized by a low S_t content, from 0.03% (Ahr) to 0.19% (Cr).

In the analysed profile, the C:S ratio decreased with depth. Lower C:S ratios in deeper soil horizons (Har – 7 and Cr – 2) suggested some accumulation of sulphides (BLOOMFIELD 1972, PRACZ 1989). This was also confirmed by the occurrence of strong reducing conditions (Eh up to -70 mV, rH 12-14). Moreover, there were no carbonates in the whole soil profile.

In the World Reference Base for Soil Resources classification (IUSS Working Group WRB 2007) *sulphide material* is distinguished, which should fulfill the following criteria: pH of 4.0 or more and 0.75 percent or more S (dry mass) and less than three times as much of calcium carbonate equivalent as S. According to these criteria, only the organic horizons characterized by neutral reaction (pH_a), lack of carbonates and rich in sulfur can be described as *sulphidic material* (Table 1). The criteria related to S_{tot} and $CaCO_3$ content are not taken into account if the material is incubated (layer 1 cm thick) under field conditions and at room temperature. Then, pH should drop by 0.5 or more units to 4.0 or less within 8 weeks.

Table 1

Selected properties of studied soil

Horizon	Depth (cm)	C_{org} (%)	N_{tot} (%)	S_{tot} (%)	C:N	C:S	pH_a	ECa (dS m^{-1})	Eh (mV)	rH	Type of material
Ha	0-22	34.5	2.559	0.78	14	44	7.0	1.77	117	18	muck
Ahr	22-36	1.35	0.092	0.03	15	54	7.6	1.43	-3	15	loose sand
Her	36-42	33.7	2.505	1.21	14	28	7.3	2.08	-70	12	low peat
Har	42-60	13.5	1.110	1.93	15	7	7.3	2.01	-50	13	mud
Cr	>60	0.33	0.021	0.19	16	2	6.9	1.48	3	14	loose sand

Abbreviations: Ha – highly decomposed organic material, Ahr – mineral horizon with accumulation of organic matter and strong reduction, Her – moderately decomposed organic material with strong reduction, Har – highly decomposed organic material with strong reduction, Cr – mineral horizon with strong reduction

Changes in selected soil properties by oxidation

Soil pH measurements were made before (pH_a, Table 1) and after sample oxidation, which was achieved by two ways. The first oxidizing agent was a 30% hydrogen peroxide solution (pH_{pox}). This method is commonly used in the WRB classification (IUSS Working Group WRB 2007) for diagnostic recognition of *sulphidic* material under the field conditions. Forced oxidation with 30% H_2O_2 should lower pH values to 2.5 or less. It should be noted that oxidation can also be influenced by the presence of organic matter or manganese compounds. Therefore, the threshold pH value is much lower than that adopted in the incubation method.

The pH_a values ranged between 6.9 to 7.6 (Figure 1). The application of H_2O_2 resulted in a significant decrease in pH values. The difference between pH_a and pH_{pox} increased with depth (from 2.5 to 6.2 pH units). In the deeper horizons, pH_a values ??below 2.5 were recorded: Her (1.1), Har (1.4) and Cr (1.6). It allowed us to identify *sulphidic* material.

The second method was the incubation of soil samples in the laboratory. During the incubation soil material is exposed to ambient conditions to simulate natural acidification behavior (SULLIVAN et al. 2009).

The pH measured on the last day of the incubation (pH_{ox}) decreased from 0.4 (Ha) to 3.1 units (Cr) compared to pH_a – Figure 1. The response to change in the soil oxidation-reduction conditions was different at individual horizons, depending on the type of material. It should be noted that in the whole profile there was no calcium carbonate, which would have buffered pH declines.

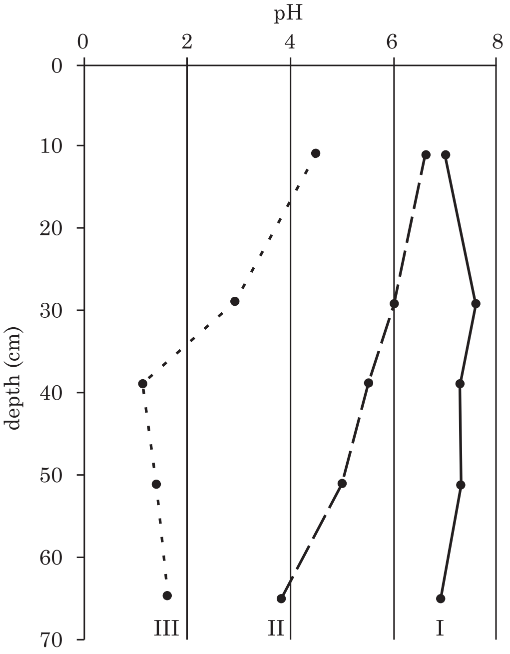


Fig. 1. Variability of soil pH in selected profile: I – before incubation (pH_a), II – after incubation (pH_{ox}), III – after oxidation by peroxide (pH_{pox})

Figure 2 presents the dynamics of soil sample oxidation. The rate of pH decline was expressed as a function of the time (ΔpH/Δt). During the incubation, certain minimum fluctuations (decrease/increase of the pH values) were noted. Namely, the variable ΔpH/Δt was greater than 0 at some points on the diagram. It can be explained by the lack of homogenization of the soil material. The fastest pH decline (already during the first three days of incubation) was recorded in sandy Cr horizon, characterized by the lowest carbon content and a relatively high content of total sulphur (C:S = 2). The value of pH_{ox} was 3.8, which allowed us to distinguish *sulphidic material*. Despite having similar texture to Cr, the oxidation test of Ahr sample gave clearly different results (pH_{ox} = 6.0). This can be linked to a higher content of Corg and lower S_{tot} (C: S = 54). In the case of organic horizons, the maximum rate of pH decline occurred after 5 days from the start of incubation. The pH_{ox} values exceeded 4.0 and thus these horizons did not fulfill the criteria for *sulphidic* material.

Finally, the biggest pH declines in the entire soil profile occurred within the first 10 days. Over the next 10 days, the fluctuations were small. However, after 20 days of analysis, relative stabilization of pH levels was recorded. Therefore, it can be concluded that almost complete oxidation of samples took place after a 4-week period of the incubation, which is shorter than recommended in the WRB classification, i.e. 8 weeks.

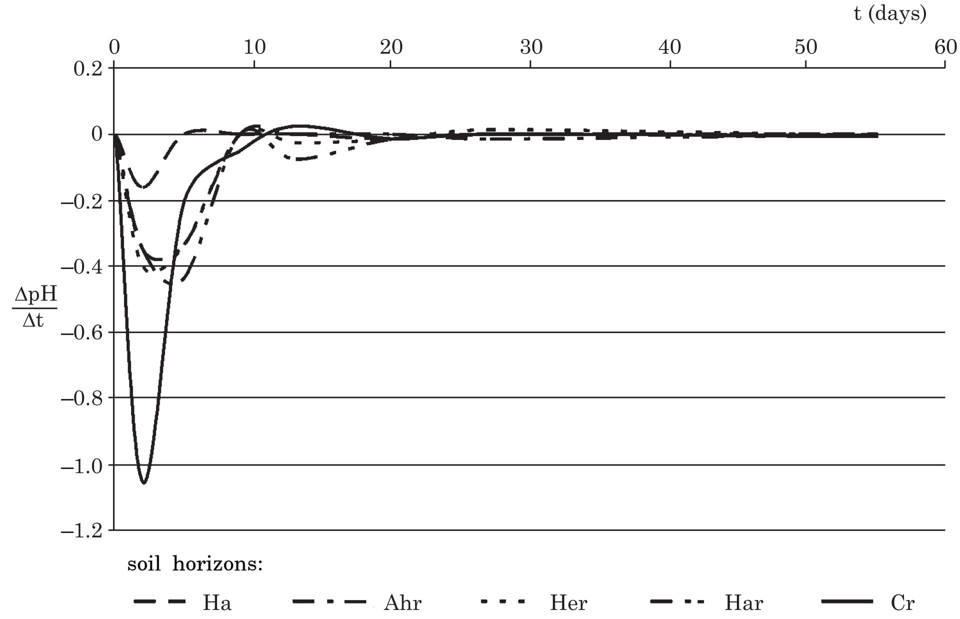


Fig. 2. Rate of pH decline caused by the soil sample incubation as a function of time

Beside the above changes in soil pH, the oxidation of sulphides causes simultaneous increase of oxidized form of sulphur, namely sulphates (VI). Comparing the results of SO_4^{2-} determinations before and after incubation, the highest increase in sulphate concentrations was observed in samples taken from organic horizons: Her (from 38.2 to 279 mg 100 g^{-1} of absolutely dry soil) and Har (from 19.7 to 131 mg 100 g^{-1} of absolutely dry soil). In Ha horizon, characterized by a relative high S_{tot} content (0.78%, Table 1), only a slight increase in SO_4^{2-} ions was noted (from 39.3 to 58.4 mg 100 g^{-1} of absolutely dry soil). The smallest changes in SO_4^{2-} concentrations appeared in mineral, poor in sulphur (S_{tot} < 0.2%) Ahr and Cr horizons (from 17.6 to 28.8 and from 10.8 do 48.3 mg 100 g^{-1} of absolutely dry soil, respectively).

Dynamics of the changes in SO_4^{2-} ion concentrations in time is shown in Figure 3. The $SO_{4x}^{2-}/SO_{4a}^{2-}$ ratio specifies how many times the content of sulphates over consecutive days of oxidation was higher than their content in the unoxidized sample. The ratio equal to 1 means that the amount of sulphates was constant during the experiment, and the soil material did not contain sulphides. The $SO_{4x}^{2-}/SO_{4a}^{2-}$ ratio for Ha and Ahr horizons ranged from 1 to about 2, while the deeper horizons (Her, Har, and Cr) were significantly richer in sulphides (4-10).

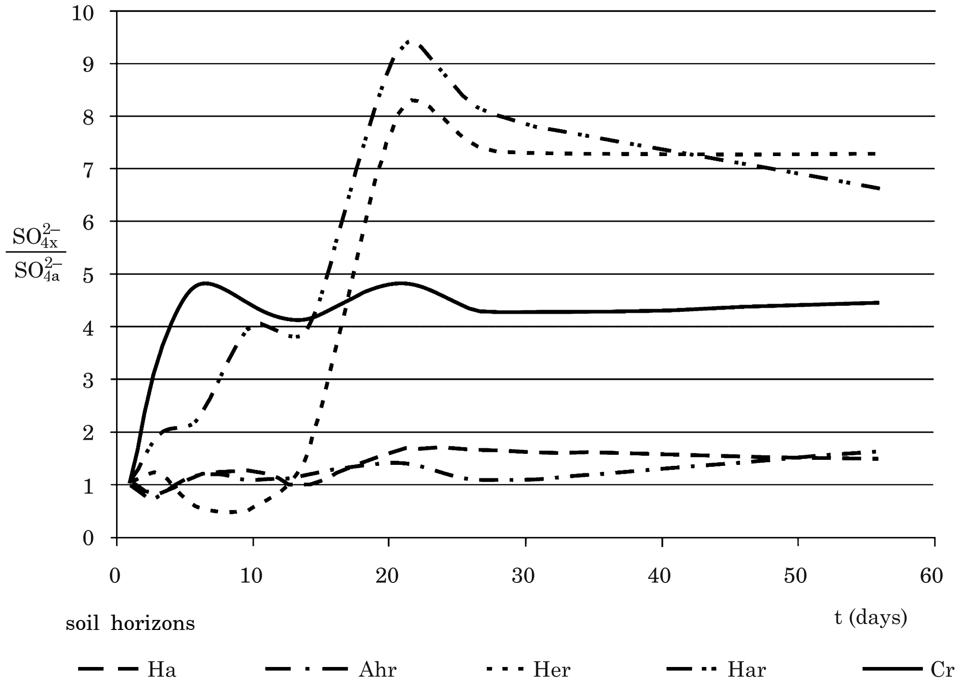
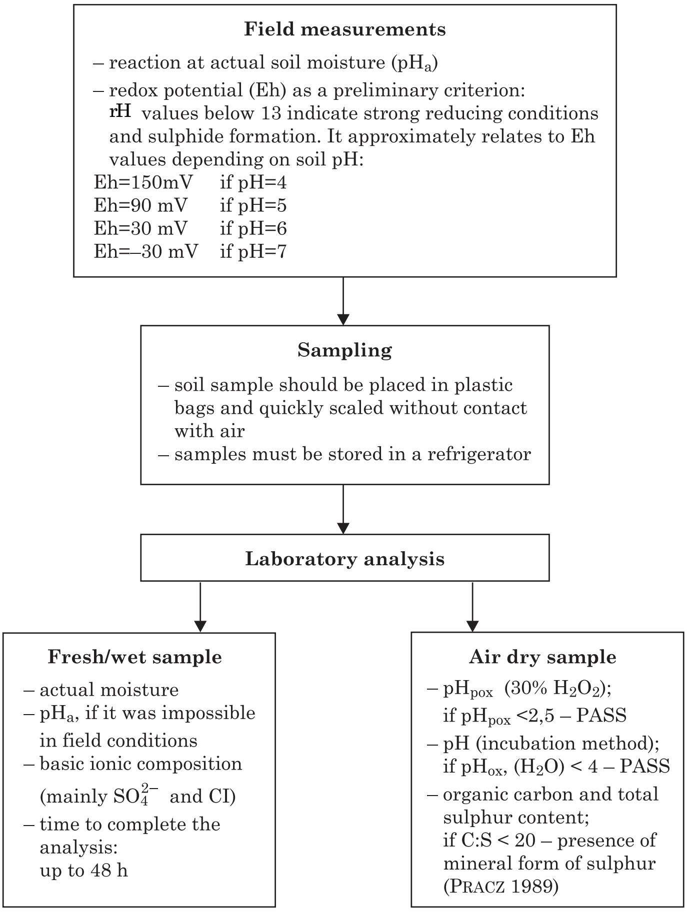


Fig. 3. Changes in the $SO_{4x}^{2-}/SO_{4a}^{2-}$ ratio as a result of sample incubation in 8 weeks

Figures 2 and 3 shows a similar dynamic changes in pH and sulphate content in the analysed soil horizons. This is understandable, given the fact that the final product of sulphide oxidation is sulphuric acid. The results suggest that the analysed soils are very sensitive to changes in redox conditions. Therefore, inadequate regulation of the groundwater level could lead to the soil degradation. This is particularly important because the studied area belongs to habitats protected under the Nature 2000 network.

However, the results of other authors indicate that soil oxidation in a laboratory gives a stronger acidification effect than oxidation caused by natural soil drainage and exposure to atmospheric oxygen (van Breemen 1973, Dent 1980, Pracz 1989). Under field conditions, the total oxidation of sulphides does not occur as quickly as in a laboratory and sulphuric acid is removed from soil by leaching (Bloomfield, Coulter 1973).



Field measurements

- reaction at actual soil moisture (pH_a)
- redox potential (Eh) as a preliminary criterion: rH values below 13 indicate strong reducing conditions and sulphide formation. It approximately relates to Eh values depending on soil pH:

Eh=150mV if pH=4
Eh=90 mV if pH=5
Eh=30 mV if pH=6
Eh=–30 mV if pH=7

Sampling

- soil sample should be placed in plastic bags and quickly scaled without contact with air
- samples must be stored in a refrigerator

Laboratory analysis

Fresh/wet sample

- actual moisture
- pH_a, if it was impossible in field conditions
- basic ionic composition (mainly SO_4^{2-} and CI)
- time to complete the analysis: up to 48 h

Air dry sample

- pH_{pox} (30% H_2O_2); if pH_{pox} <2,5 – PASS
- pH (incubation method); if pH_{ox}, (H_2O) < 4 – PASS
- organic carbon and total sulphur content; if C:S < 20 – presence of mineral form of sulphur (Pracz 1989)

Fig. 4. Proposed methodical procedure in studies of AASS

Methodical remarks

Soils containing reduced forms of sulphur (mainly iron sulphides), due to their specific characteristics, require a special methodological approach. It should particularly take into account the unique sensitivity of these soils to changes in redox conditions (groundwater level), resulting in relatively rapid acidification.

The methodical procedure for PASS, which includes both field and laboratory work, is proposed below (Figure 4). Such a methodical approach has not yet been presented in Poland.

CONCLUSIONS

1. During the incubation of soil organic horizons, characterized by a relatively high content of total sulphur (> 0.75%), pH did not decrease below 4 as a result of oxidation. The opposite effect was observed in the case of sandy horizons, poor in sulphur.

2. The rate of pH decline and the increase in sulphate concentrations during ther incubation were the highest in the initial period of the sample oxidation, which justifies the need to perform some analysis in samples of fresh /wet within 48 hours of sampling.

3. According to the WRB classification (2007), both types of the analysed soil horizons, despite the different characteristics, fulfilled the diagnostic criteria for *sulphidic* material.

4. Soils containing reduced forms of sulphur (mainly iron sulphides), due to their specific characteristics, require a special methodical approach. A possible solutions could be the proposed procedure involving both field and laboratory work.

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